Proposed definitions of the correlation energy density from a Hartree-Fock starting point: The two-electron Moshinsky model atom as an exactly solvable model

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In both molecular physics and condensed matter theory, deeper understanding of the correlation energy density $\epsilon_c(\mathbf{r})$ remains a high priority. By adopting Löwdin's definition of correlation energy as the difference between the exact and the Hartree-Fock values, here we propose two alternative routes to define this. One of these involves both exact and Hartree-Fock (HF) wavefunctions, while the second requires a coupling constant integration. As an exact analytical example of the first route, we treat the two-electron model atom of Moshinsky, for which both confinement potential and interactions are harmonic. Though the correlation energy density $\epsilon_c(\mathbf{r})$ is known analytically, we also investigate numerically its relation to the exact ground-state density in this example.

I. INTRODUCTION

It is true to say that one of the remaining problems in both molecular physics and condensed matter theory is to gain deeper understanding of the correlation energy density. We have recently approached this problem via Møller-Plesset (MP) perturbation theory [1, 2]. By adopting Löwdin's [3] definition of the ground-state correlation energy as the difference between the exact and the Hartree-Fock (HF) values, here we shall propose two, formally exact, routes to the correlation energy density. The first of these, as in [2], starts out from the so-called level-shift formula [4], but in contrast to [2], where low-order perturbation theory is invoked, our central example is exactly solvable, which means that the MP series has been summed to all orders. This example is the model two-electron atom introduced by Moshinsky [5] and it is therefore natural enough that we pose the two-electron atom example formally exactly in section II immediately below. Section III presents the exact theory for the Moshinsky model. Comparison is made in section IV of the total kinetic energy, including correlation of the Moshinsky atom with that of the (non-relativistic) He-like series of atomic ions for large atomic number. An alternative route for defining the correlation energy density is then proposed in section V, which may prove

to come into its own in solid-state theory rather than molecular physics. Section VI constitutes a summary, plus proposals for future studies which should be fruitful.

II. EXACT LEVEL-SHIFT THEORY FOR THE GROUND STATE OF ATOMS AND MOLECULES

Let us consider an N-body system described by the Hamiltonian

$$H = H_0 + H_I, \tag{1a}$$

$$H_0 = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \Psi^\dagger(\mathbf{r}_1) h(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}), \tag{1b}$$

$$H_I = \frac{1}{2} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \Psi^\dagger(\mathbf{r}_1) \Psi^\dagger(\mathbf{r}_2) v(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_2) \Psi(\mathbf{r}_1) \tag{1c}$$

where the field operators in second quantization are defined as usual by their expressions in terms of the creation and annihilation operators and their standard commutation relations:

$$\Psi(\mathbf{r}) = \sum_k \Psi_k(\mathbf{r}) a_k, \tag{2a}$$

$$\Psi^\dagger(\mathbf{r}) = \sum_k \Psi_k^*(\mathbf{r}) a_k^\dagger, \tag{2b}$$

$$[a_k, a_{k'}^\dagger]_+ = \delta_{kk'}, \quad [a_k, a_{k'}]_+ = 0. \tag{2c}$$

Here, $v(\mathbf{r}_1, \mathbf{r}_2)$ is the interaction potential between the particles and $h(\mathbf{r}_1, \mathbf{r}_2)$ is the kernel of a one particle operator that reduces to the kinetic energy operator in the

usual cases. However, it may also embody the effect of an external potential and other effects. The creation (annihilation) operator $a_k^\dagger$ (a_k) is assumed to create (annihilate) particles in states described by the wave-functions $\Psi_k(\mathbf{r})$. Here, as is usual, $\mathbf{r} \equiv (\mathbf{x}, s)$, with $\mathbf{x}$ denoting the particle position, and s the particle spin, and k is the collective quantum number associated with the basis states $\{\Psi_k\}$. We will assume that the free Hamiltonian is diagonal in the spin variable and also that the interaction is spin-independent, *i.e.*

$$h(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{x}_1, \mathbf{x}_2)\delta_{s_1 s_s} \tag{3a}$$
$$v(\mathbf{r}_1, \mathbf{r}_2) = v(\mathbf{x}_1, \mathbf{x}_2). \tag{3b}$$

Following [2], let us use the level-shift formula [4], taking as the unperturbed problem the Fock Hamiltonian H_{HF}, with ground state energy E_0. Then, for two electrons, we can write explicitly for the correlation energy density $\epsilon_c(\mathbf{r}_1)$

$$\epsilon_c(\mathbf{r}_1) = \frac{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2)[H - H_{\mathrm{HF}}]\Phi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2}{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2)\Phi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2}, \tag{4}$$

where Ψ is the exact ground-state wave function. It should be noted that the definition above of the correlation energy density, Eq. (4), is not unique. However, this circumstance is not necessarily problematic, because any alternative definition should lead to the same total integrated correlation energy. This is a similar situation, and moreover also seems to be close connected, with the known lack of precise definitions of the energy-momentum tensor for general physical systems. Therefore, such a property should not restrict the value and utility of the concept, whenever it becomes possible to construct a theoretical scheme in which this energy density plays a relevant role independently of its non-unique definition. From Eq. (4) we then have, in an obvious notation

$$\langle \Psi | \Phi_{\mathrm{HF}} \rangle \epsilon_c(\mathbf{r}_1) = E \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2)\Phi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2$$
$$- E_0 \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2)\Phi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2, \tag{5}$$

where in reaching Eq. (5) from Eq. (4), H has been allowed to act on Ψ^*, and H_{HF} on Φ_{HF}. Of course, by integrating both sides of Eq. (5) over all $\mathbf{r}_1$, we obtain a trivial identity for $E - E_0$, the latter quantity being simply the total Löwdin correlation energy $E_c = \int \epsilon_c(\mathbf{r})d\mathbf{r}$.

While Eq. (5) is of course, valid for the (nonrelativistic) He-like series of two-electron ions with atomic number Z, we do not presently know Ψ^* and E analytically. Therefore in section III immediately below, we turn to illustrate Eq. (5) analytically by appeal to the Moshinsky two-electron atom model [5].

III. EXACT USE OF THE LEVEL-SHIFT FORMULA FOR THE HARMONIC MOSHINSKY TWO-ELECTRON MODEL

The Moshinsky model atom has confining (external) potential $\frac{1}{2}(|\mathbf{r}_1|^2 + |\mathbf{r}_2|^2)$ and particle interaction also of harmonic form $\frac{1}{2}k|\mathbf{r}_1 - \mathbf{r}_2|^2$. Using coordinates $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}$ and $\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2)/\sqrt{2}$, the exact ground-state wavefunction takes the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \frac{(1 + 2k)^{\frac{3}{8}}}{\pi^{\frac{3}{2}}} \exp\left(-\frac{1}{2}\mathbf{R}^2\right) \exp\left(-\frac{1}{2}(1 + 2k)^{\frac{1}{2}}\mathbf{r}^2\right). \tag{6}$$

Less well known is the fact that the corresponding Φ_{HF} wavefunction entering the key expression (5) for the correlation energy density has the exact form [6]

$$\Phi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2), \tag{7}$$

where

$$\phi(\mathbf{r}) = \frac{(1 + k)^{\frac{3}{8}}}{\pi^{\frac{3}{4}}} \exp\left(-\frac{1}{2}(1 + k)^{\frac{1}{2}}\mathbf{r}^2\right). \tag{8}$$

It is understood that Eq. (7) only provides the spatial dependence of the ground state, whose overall antisymmetric character is to be provided by the spin dependence. Since the spin structure of the ground state problem is fixed by its singlet character, we can safely employ the symbol $\mathbf{r}$ below to denote only the spatial coordinates.

Plots of the "overlap" $\langle \Psi | \Phi_{\mathrm{HF}} \rangle$ are already available as functions of the particle-particle interaction strength k: *e.g.* for $k = 1$ the overlap is 0.94. Inserting Eqs. (6) and (7) into the right-hand-side of Eq. (5) we obtain an exact result for $\epsilon_c(\mathbf{r})$, now spherically symmetric in the Moshinsky atom model. The correlation energy density, the HF, and exact electron densities, respectively, have all the analytic form

$$\epsilon_c(\mathbf{r}) = E_c \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \exp(-\alpha r^2), \quad \alpha = \frac{b^2 - (1 - a)^2}{4b}, \tag{9a}$$

$$\rho(\mathbf{r}) = 2\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \exp(-\beta r^2), \quad \beta = \frac{2a}{1 + a}, \tag{9b}$$

$$\rho_{\mathrm{HF}}(\mathbf{r}) = 2\left(\frac{\gamma}{\pi}\right)^{\frac{3}{2}} \exp(-\gamma r^2), \quad \gamma = \sqrt{1 + k}, \tag{9c}$$

$$a = \sqrt{1 + 2k}, \quad\quad b = 1 + a + 2\gamma. \tag{9d}$$

Notice that all three functions are gaussians, albeit with a different decay rate exponent. Figure 1 exhibits the k-dependence of the latter. At $k = 0$ the interaction vanishes, and all three coefficients equal one. As the interaction is turned on they increase, departing slowly from each other. Figure 2 shows the reduced correlation energy density $\epsilon_c(\mathbf{r})/E_c$ (full line) together with the HF (long dashes) and exact (short dashes) densities normalized to one, for $k = 1$. It is apparent from the functional identity and the weak parameter divergence that there
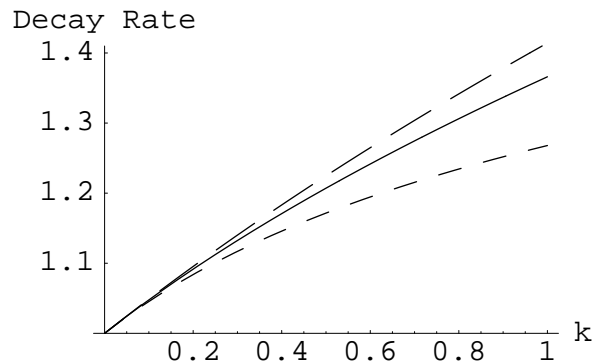
Decay Rate

FIG. 1: Decay rate for the correlation energy density (α, full line), and the exact (β, short dashed) and Hartree-Fock (γ, long dashed) one-particle densities, in terms of the coupling parameter k (All quantities are in atomic units).
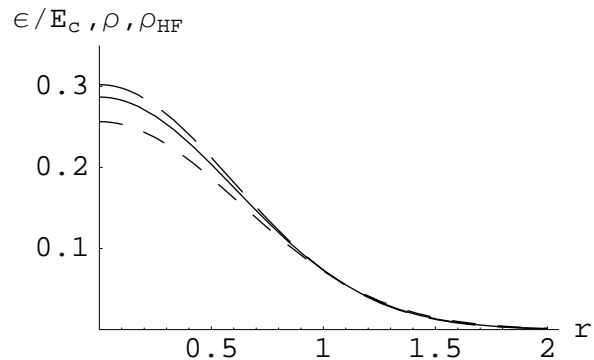
$\epsilon / E_c, \rho, \rho_{HF}$

FIG. 2: Radial dependence of the reduced correlation energy density (full line), exact (short dashed) and Hartree-Fock (long dashed) particle densities. Here, $k = 1$. All quantities are in atomic units.

is an intimate connection between the correlation energy density and the exact or HF electron densities. This result is compatible with the definition of $\epsilon_c(\mathbf{r})$ as proportional to the HF one particle density, as proposed in [2]. Exact relations for the Moshinsky model are presented in the Appendix.

IV. DENSITY DEPENDENCE OF THE TOTAL KINETIC ENERGIES IN THE MOSHINSKY MODEL ATOM AND THE He-LIKE ATOMIC IONS AT LARGE ATOMIC NUMBER Z

Let us illustrate in this section two examples of physical systems in which the total kinetic energy can be expressed as a functional of the density. We note first that the total kinetic energy of the Moshinsky model treated in section III above can be expressed exactly in terms solely of $\rho(\mathbf{r})$. From [7] one knows that the kinetic energy density t now defined from the wavefunction form

$(\nabla \Psi)^2$ is given by

$$t_{\text{Mosh}}(\mathbf{r}) = \frac{1}{2}\rho(\mathbf{r})\left[\frac{3}{2}\frac{(d-1)^2}{d} - \frac{2d-1}{d}\log\frac{\rho(\mathbf{r})}{\rho(\mathbf{0})}\right], \quad (10)$$

where

$$d^{-1} = 2 - \pi\left[\frac{\rho(\mathbf{0})}{2}\right]^{\frac{2}{3}}. \quad (11)$$

As noted earlier, in the Moshinsky atom the ground state $\rho(\mathbf{r})$ is purely Gaussian. Notice that, in contrast to the He-ions at large Z, to be discussed below, there is a $\log\rho(\mathbf{r})$ term. Because everything is harmonic we expect that the potential energy U will coincide with the kinetic term T and that both will be a half of the total energy E, that is

$$T = U = \frac{E}{2}. \quad (12)$$

Thus the correlation energy density can be obtained as

$$E_{\text{corr}} \simeq 2T_{\text{corr}} = 2\int t_{\text{corr}}(\mathbf{r})d\mathbf{r}. \quad (13)$$

Here, $t_{\text{corr}}(\mathbf{r}) = t_{\text{Mosh}}(\mathbf{r}) - \epsilon_{\text{HF}}(\mathbf{r})/2$, and $\epsilon_{\text{HF}}(\mathbf{r})/2$ is defined as a density of HF energy constructed from one of its expressions as spatial integrals. In such a way, the correlation energy density is defined as $\epsilon_c(\mathbf{r}) = 2t_{\text{corr}}(\mathbf{r})$.

1. Kinetic energy, including correlation, of the He-like atomic ions with large atomic number

Following the work of Schwartz [8] on the He-like atomic ions with large Z (however, still non-relativistic) the total kinetic energy T has been obtained by Gal, March and Nagy [9] as

$$T = -\frac{1}{2}\left[\frac{\rho'(\mathbf{r})}{\rho(\mathbf{r})}\right]_{\mathbf{r}=0}\int\frac{\rho(\mathbf{r})}{|\mathbf{r}|}d\mathbf{r} - \frac{1}{8}\left[\frac{\rho'(\mathbf{r})}{\rho(\mathbf{r})}\right]_{\mathbf{r}=0}^2\int\rho(\mathbf{r})d\mathbf{r}. \quad (14)$$

This expression for the total kinetic energy, again including kinetic correlation energy is evidently determined therefore solely by $\rho(\mathbf{r})$ and the derivative of $\log\rho(\mathbf{r})$. Thus, the total kinetic energy density $t(\mathbf{r})$ takes the form

$$t(\mathbf{r}) = -\frac{1}{2}\left[\frac{\rho'(\mathbf{r})}{\rho(\mathbf{r})}\right]_{\mathbf{r}=0}\frac{\rho(\mathbf{r})}{|\mathbf{r}|} - \frac{1}{8}\left[\frac{\rho'(\mathbf{r})}{\rho(\mathbf{r})}\right]_{\mathbf{r}=0}^2\rho(\mathbf{r}). \quad (15)$$

In closing this section we emphasize that in contrast to the Moshinsky atom, the total kinetic energy including correlation now depends on both $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$.

V. DIFFERENTIAL SECOND-ORDER DENSITY MATRIX FORMULA FOR CORRELATION ENERGY DENSITY VIA A COUPLING CONSTANT INTEGRATION

The differential level shift formula (4) for the correlation energy density $\epsilon_c(\mathbf{r})$ is entirely appropriate for two-electron systems like the Moshinsky atom. But repeated

volume integrations make it unwieldy for N-electron problems, with $N > 2$. Therefore, in this section we derive an alternative route via a coupling constant integration. This leads to a formula for the Löwdin correlation energy density $\epsilon_c(\mathbf{r})$ characterized by second-order density matrices. Since the development of efficient methods for the evaluation of second-order density matrices is in rapid progess, the reduced number of integrals to be evaluated can represent a helpful technical advancement, once the expressions for the density matrices are already at hand.

A. Introductory example of uniform electron liquid

To point the way, let us consider the homogeneous electron liquid (HEL). As emphasized in early work, one of us [10, 11] has used as the 'coupling constant' the mean interelectronic separation r_s. A variant of Hellmann-Feynman theorem enables to express the ground-state energy for the HEL (see e.g. [12] for a review). In particular, the ground-state energy per electron, $E(r_s)$, satisfies the virial theorem [10]

$$2T(r_s) + U(r_s) = -r_s \frac{dE}{dr_s} \qquad (16)$$

where T and U represent kinetic and potential contributions, respectively. As shown by March and Young [11], removing $T = E - U$ from Eq. (16) allows the resulting first-order differential equation for $E(r_s)$ to be integrated to yield

$$E(\lambda) = -\lambda \int^{\lambda} \frac{U(\lambda)}{\lambda^2} d\lambda, \qquad (17)$$

where $\lambda = r_s^2$ plays the role of a coupling constant adiabatically connecting the unperturbed and the exact Hamiltonians, as in Hellmann-Feynman theorem. But it is well known that $E_{\mathrm{HF}}(r_s) = (A/r_s^2) - (B/r_s)$, with $A = \frac{3}{5}$ and $B = \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}$. Hence $E(\lambda) - E_{\mathrm{HF}}$ is known via a coupling constant integration. In HEL, U is determined by the diagonal element of the second-order density matrix, and hence we seek next a generalization of

such a formula for the Löwdin correlation energy for an N-electron system without the translational invariance of the HEL.

B. Coupling constant formula

Motivated by the above HEL example, we have gone back to the treatment by Stanton [13] of the Löwdin correlation energy $E - E_{\mathrm{HF}}$ in terms of such a coupling constant integration. We write the Hamiltonian as

$$H(\lambda) = H_{\mathrm{HF}} + \lambda H_1, \qquad (18)$$

where $0 \leq \lambda \leq 1$ is a coupling constant adiabatically connecting the HF Hamiltonian to the exact Hamiltonian $H \equiv H(\lambda = 1)$. Stanton [13] then generalizes Hellmann-Feynman's theorem to embrace the case of an N-particle Hamiltonian. Beginning with the elementary identity $E - E_{\mathrm{HF}} \equiv E(1) - E(0) = \int_0^1 (dE(\lambda)/d\lambda)d\lambda$, Eq. (12) in Ref. [13] reads, in obvious notation,

$$E - E_{\mathrm{HF}} = \int_0^1 [\langle\Psi(\lambda)|\frac{\partial H}{\partial \lambda}|\Psi(\lambda)\rangle - \langle\Phi_{\mathrm{HF}}|\frac{\partial H}{\partial \lambda}|\Phi_{\mathrm{HF}}\rangle]d\lambda, \qquad (19)$$

where $\Psi(\lambda)$ is the ground-state eigenvector of the exact Hamiltonian $H(\lambda)$ with eigenvalue $E(\lambda)$, and Φ_{HF} is the HF ground-state with energy E_{HF}. The scalar products $\langle\ldots\rangle$ obviously imply an integration over the coordinates of N particles. The important point to stress here is that instead of the quantum-mechanical average $\langle\Psi|H|\Phi_{\mathrm{HF}}\rangle$ entering the level shift formula, Eq. (4), Eq. (19) involves 'symmetric' averages like $\langle\Psi|H|\Psi\rangle$ and $\langle\Phi_{\mathrm{HF}}|H|\Phi_{\mathrm{HF}}\rangle$. These, of course, are achieved at the cost of the coupling constant integration. But since $H(\lambda = 1)$ involves only one- and two-body operators, all the volume integrations but two for an N-electron atom, molecule of cluster can be achieved by use of the second-order density matrix $\Gamma(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2')$ defined by [3]

$$\Gamma(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2') = \frac{N(N-1)}{2} \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N) \Psi(\mathbf{r}_1', \mathbf{r}_2', \mathbf{r}_3, \ldots \mathbf{r}_N) d\mathbf{r}_3 \ldots d\mathbf{r}_N. \qquad (20)$$

Inserting Eq. (20) into Eq. (19) we hence find

$$E - E_{\mathrm{HF}} = \frac{2}{N(N-1)} \int_0^1 d\lambda \int d\mathbf{r}_1 d\mathbf{r}_2 \left[h(\mathbf{r}_1', \mathbf{r}_2') - h_{\mathrm{HF}}(\mathbf{r}_1', \mathbf{r}_2')\right] \Gamma(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2'; \lambda)|_{\mathbf{r}_1'=\mathbf{r}_1, \mathbf{r}_2'=\mathbf{r}_2}, \qquad (21)$$

where use has been made of the following results:

$$\frac{\partial H(\lambda)}{\partial \lambda} = H_1 = H - H_{\text{HF}} \tag{22a}$$

$$\langle \Phi_{\text{HF}} | \frac{\partial H(\lambda)}{\partial \lambda} | \Phi_{\text{HF}} \rangle = \langle \Phi_{\text{HF}} | H - H_{\text{HF}} | \Phi_{\text{HF}} \rangle = 0. \tag{22b}$$

In Eq. (21), the kernel $h(\mathbf{r}_1', \mathbf{r}_2')$ associated with the 'free' Hamiltonian has been defined in Eq. (3a), whereas the expression of the Hartree-Fock kernel $h_{\text{HF}}(\mathbf{r}_1', \mathbf{r}_2')$ will be given by Eq. (25) below.

The final step, as with the level shift formula Eq. (4), is to drop the volume integration over $\mathbf{r}_2$ and hence to achieve the desired result for the Löwdin correlation energy density $\epsilon_c(\mathbf{r}_1)$ as the coupling constant integration over second-order density matrices as

$$\epsilon_c(\mathbf{r}_1) = \frac{2}{N(N-1)} \int_0^1 d\lambda \int d\mathbf{r}_2 \left[h(\mathbf{r}_1', \mathbf{r}_2') - h_{\text{HF}}(\mathbf{r}_1', \mathbf{r}_2') \right] \Gamma(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2'; \lambda) \big|_{\mathbf{r}_1' = \mathbf{r}_1, \mathbf{r}_2' = \mathbf{r}_2}, \tag{23}$$

The explicit form of the HF kernel $h_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (23) can be written as

$$h_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{r}_1, \mathbf{r}_2)$$
$$+ \delta(\mathbf{r}_1 - \mathbf{r}_2) \int d\mathbf{r}_3 v(\mathbf{r}_1, \mathbf{r}_3) \sum_k \Psi_k^*(\mathbf{r}_3) \Psi_k(\mathbf{r}_3)$$
$$- v(\mathbf{r}_1, \mathbf{r}_2) \sum_k \Psi_k(\mathbf{r}_1) \Psi_k^*(\mathbf{r}_2), \tag{24}$$

where the sum over k runs over the filled orbitals of the mean field problem. After explicitly writing the spin and spatial dependence, this expression takes the form

$$h_{\text{HF}}(\mathbf{x}_1, s_1; \mathbf{x}_2, s_1) = h(\mathbf{x}_1, \mathbf{x}_2) \delta_{s_1 s_2}$$
$$+ \delta_{s_1 s_2} \delta(\mathbf{x}_1 - \mathbf{x}_2) \sum_{s_3 = \pm 1} \int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) \sum_k \Psi_k^*(\mathbf{x}_3, s_3) \Psi_k(\mathbf{x}_3, s_3)$$
$$- v(\mathbf{x}_1, \mathbf{x}_2) \sum_k \Psi_k(\mathbf{x}_1, s_1) \Psi_k^*(\mathbf{x}_2, s_2), \tag{25}$$

where the single particle orbitals Ψ_k satisfy the HF equations

$$\int d\mathbf{r}_2 h_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \Psi_k(\mathbf{r}_2) = \epsilon_k \Psi_k(\mathbf{r}_1). \tag{26}$$

Now, the second-quantized HF Hamiltonian can be expressed as

$$H_{\text{HF}} = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \Psi^\dagger(\mathbf{r}_1) h_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_2) - \sum_k \frac{1}{2} v_k$$

$$= \sum_k \epsilon_k a_{k'}^\dagger a_k - \sum_k \frac{1}{2} v_k \tag{27a}$$

$$\epsilon_k = h_k + v_k \tag{27b}$$

$$h_k = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \Psi_k^*(\mathbf{r}_1) h(\mathbf{r}_1, \mathbf{r}_2) \Psi_k(\mathbf{r}_2), \tag{27c}$$

$$v_k = \sum_{k'} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \Psi_k^*(\mathbf{r}_1) \Psi_{k'}^*(\mathbf{r}_2) v(\mathbf{r}_1, \mathbf{r}_2) \left(\Psi_k(\mathbf{r}_1) \Psi_{k'}(\mathbf{r}_2) - \Psi_{k'}(\mathbf{r}_1) \Psi_k(\mathbf{r}_2) \right). \tag{27d}$$

It should be noted that the field operator $\Psi(\mathbf{r})$ in the above expressions are now constructed in terms of the single particle mean field orbitals. It should also be re-

called that in general the kernel $h_{\mathrm{HF}}(\mathbf{r}_1', \mathbf{r}_2')$ is not simply given by the Fock operator. It should also incorporate an additive constant which implements the property

$$\langle \Phi_{\mathrm{HF}} | H_{\mathrm{HF}} | \Phi_{\mathrm{HF}} \rangle = \langle \Phi_{\mathrm{HF}} | H | \Phi_{\mathrm{HF}} \rangle = E_{\mathrm{HF}}. \qquad (28)$$

A possible optional form for H_{HF} could be the one introduced in Ref. [1] in order to propose an improvement of the Møller-Plesset perturbative expansion. In this approach the above mentioned additive constant is not required and the second quantized version of H_{HF} becomes a pure bilinear form in the creation and anihilation operators.

We can, so far, only see a way to evaluate Eq. (23) wholly analytically for the two-electron Moshinsky atom. But we have not pressed the details of that ourselves, since for this simple two-electron model the level shift formula has overwhelming advantages over the coupling constant integration formula. But with recent progress in evaluating correlated two-body density matrices for systems with $N > 2$, we expect Eq. (23) to rapidly become the advantageous route to employ [14]. Therefore, in App. B, we present an alternative method based on the Green function.

VI. SUMMARY AND FUTURE DIRECTIONS

The two proposals made here for the correlation energy density $\epsilon_c(\mathbf{r}_1)$ are embodied in Eqs. (5) and (23). The first one involves knowledge of the exact many-electron ground-state function Ψ, which of course is generally not available. For the Moshinsky two-electron atom model, however, both Ψ and its HF counterpart are known. Our results show that the functional form of the correlation energy density, HF and exact density is the same, in support of a simple proportionality expression.

The second proposal has a more general character. An integration over a coupling constant λ involving the second order density matrix must be accomplished. This alternative seems promising for solid state applications. However, we delay its analysis for further extensions of this work. The homogenous electron liquid case of the so-called Sawada Hamiltonian (see [15]) would appear then to afford a promising starting point.

Finally, returning to the level shift, the early analytical work of Schwartz [8] on He-like atomic ions with large Z referred to in section 4, may provide further insight into the use of the differential level shift formula (4). This formula, of course, is readily generalized beyond this two-electron example, but applications then are likely to involve considerable computational effort.
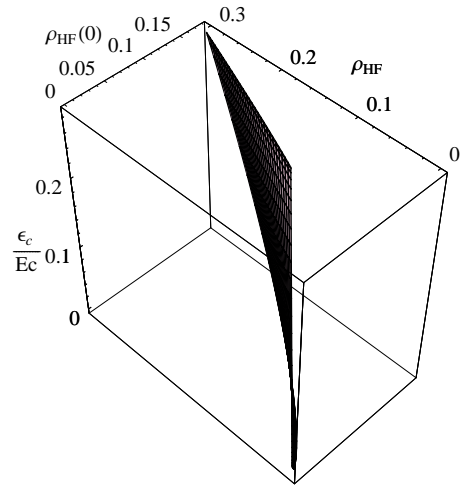
Acknowledgments

FIG. 3: Reduced correlation energy density for the Moshinsky model as a function of the Hartree-Fock density, for a range of values of the latter evaluated at the origin. All quantities are in atomic units.

APPENDIX A: DEPENDENCE OF REDUCED CORRELATION ENERGY ON THE ELECTRON DENSITY

This Appendix is motivated by the simple observation that, for the Moshinsky model, where we know both the exact electron density $\rho(r)$ and the HF counterpart $\rho_{\mathrm{HF}}(r)$, we expect the difference $\rho(r) - \rho_{\mathrm{HF}}(r)$ to depend on the reduced correlation energy density $\epsilon_c(\mathbf{r})/E_c$.

We have from Eqs. (9a) and (9c) in the main text, that

$$\rho(\mathbf{r}) = \rho(0)\exp(-\beta r^2), \qquad (A1)$$
$$\rho_{\mathrm{HF}}(\mathbf{r}) = \rho_{\mathrm{HF}}(0)\exp(-\gamma r^2). \qquad (A2)$$

Hence,

$$\rho(\mathbf{r}) - \rho_{\mathrm{HF}}(\mathbf{r}) = \rho(0)(\exp(-r^2))^{\beta} - \rho_{\mathrm{HF}}(0)(\exp(-r^2))^{\gamma}. \qquad (A3)$$

But we also have

$$\frac{\epsilon_c(\mathbf{r})}{E_c} = \frac{\epsilon_c(0)}{E_c}(\exp(-r^2))^{\alpha}. \qquad (A4)$$

Hence from Eq. (A4) we can write

$$\exp(-r^2) = \left(\frac{\epsilon_c(\mathbf{r})}{\epsilon_c(\mathbf{0})}\right)^{\frac{1}{\alpha}}. \qquad (A5)$$

Substituting this equation into Eq. (A3) we find,

$$\rho(\mathbf{r}) - \rho_{\mathrm{HF}}(\mathbf{r}) = \rho(0)\left(\frac{\epsilon_c(\mathbf{r})}{\epsilon_c(\mathbf{0})}\right)^{\frac{\beta}{\alpha}} - \rho_{\mathrm{HF}}(0)\left(\frac{\epsilon_c(\mathbf{r})}{\epsilon_c(\mathbf{0})}\right)^{\frac{\gamma}{\alpha}}. \tag{A6}$$

This appears to be a functional relation between $\epsilon_c(\mathbf{r})/\epsilon_c(\mathbf{0})$ and $\rho(\mathbf{r}) - \rho_{\mathrm{HF}}(\mathbf{r})$. But of course, on the RHS, the four quantities $\rho(0)$, $\rho_{\mathrm{HF}}(0)$, γ/α and β/α all depend on the interaction strength k. However, one of these four quantities is sufficient to carry the fingerprints of k for the others: we single out therefore $\rho_{\mathrm{HF}}(0)$. But $\rho(0)$ and $\rho_{\mathrm{HF}}(0)$ are known from normalization of the densities to two. Hence we can write,

$$\frac{\rho(0)}{\rho_{\mathrm{HF}}(0)} = \left(\frac{\beta}{\gamma}\right)^{\frac{3}{2}}. \tag{A7}$$

and also

$$\rho(\mathbf{r}) = \rho(0)(\exp(-r^2))^{\beta} \tag{A8}$$

plus

$$\rho_{\mathrm{HF}}(\mathbf{r}) = \rho_{\mathrm{HF}}(0)(\exp(-r^2))^{\gamma} \tag{A9}$$

From the latter equations it follows that

$$\rho(\mathbf{r}) = \rho_{\mathrm{HF}}(\mathbf{0})\left(\frac{\beta}{\gamma}\right)^{\frac{3}{2}}\left(\frac{\rho_{\mathrm{HF}}(\mathbf{r})}{\rho_{\mathrm{HF}}(\mathbf{0})}\right)^{\frac{\beta}{\gamma}} \tag{A10}$$

Substituting this equation in Eq. (A6) yields

$$\left(\frac{\beta}{\gamma}\right)^{\frac{3}{2}}\left(\frac{\rho_{\mathrm{HF}}(\mathbf{r})}{\rho_{\mathrm{HF}}(\mathbf{0})}\right)^{\frac{\beta}{\gamma}} - \frac{\rho_{\mathrm{HF}}(\mathbf{r})}{\rho_{\mathrm{HF}}(\mathbf{0})} =$$
$$\left(\frac{\beta}{\gamma}\right)^{\frac{3}{2}}\left(\frac{\epsilon_c(\mathbf{r})}{\epsilon_c(\mathbf{0})}\right)^{\frac{\beta}{\alpha}} - \left(\frac{\epsilon_c(\mathbf{r})}{\epsilon_c(\mathbf{0})}\right)^{\frac{\gamma}{\alpha}}. \tag{A11}$$

Notice that the strength of the interaction does not appear explicitly in this formula. Figure 3 shows a three dimensional plot of $\epsilon_c(\mathbf{r})/\epsilon_c(\mathbf{0})$, $\rho_{\mathrm{HF}}(\mathbf{r})$ and $\rho_{\mathrm{HF}}(\mathbf{0})$, where the latter plays the role of the interaction strength k.

APPENDIX B: COUPLING CONSTANT INTEGRATION IN A GREEN FUNCTION FORMULA

Following the discussion of Fetter and Walecka [16], we here attempt to solve the time-independent Schrödinger equation for an arbitrary value of λ, namely

$$H(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda), \tag{B1}$$

where the wave function Ψ is assumed to be normalized: that is $\langle\Psi(\lambda)|\Psi(\lambda)\rangle = 1$. One immediately finds then from Eq. (B1) that

$$E(\lambda) = \langle\Psi(\lambda)|H(\lambda)|\Psi(\lambda)\rangle. \tag{B2}$$

Differentiating with respect to the parameter λ yields

$$\frac{d}{d\lambda}E(\lambda) = \langle\Psi(\lambda)|H_1|\Psi(\lambda)\rangle, \tag{B3}$$

where $H_1 = H(\lambda = 1) - H_{\mathrm{HF}}$, in the present study. Integrating this expression produces

$$E - E_0 = \int_0^1 \frac{d\lambda}{\lambda}\langle\Psi(\lambda)|\lambda H_1(\lambda)|\Psi(\lambda)\rangle. \tag{B4}$$

Hence again one is led to a level-shift formula, with E_0 denoting the HF ground state energy but now via the coupling constant integration in Eq. (B4).

Fetter and Walecka then display the way in which Eq. (B4), for N electrons, can be reduced to integrations over just two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, by means of a time-dependent Green function, denoted now by $G^{\lambda}(\mathbf{r}_1, t; \mathbf{r}_2, t')$. This result, shown in their equation (7.31), then reads

$$E - E_{\mathrm{HF}} = \pm\frac{i}{2}\int_0^1 \frac{d\lambda}{\lambda}\int d\mathbf{r}_1 \lim_{t'\to t^+}\lim_{\mathbf{r}_2\to\mathbf{r}_1}\left[\int d\mathbf{y}\delta(\mathbf{r}_1 - \mathbf{y})\left(i\hbar\frac{\partial}{\partial t} - h_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{y})\right)\mathrm{Tr}\,G^{\lambda}(\mathbf{y}, t; \mathbf{r}_2, t')\right], \tag{B5}$$

where in place of the kinetic energy operator, in our case the Fock operator h_{HF} appears. As with the level-shift formula in section II, we now take the differential form of Eq. (B5) to find the second result proposed in the present study for the correlation energy density $\epsilon_c(\mathbf{r})$, namely

$$\epsilon_c(\mathbf{r}_1) = \pm\frac{i}{2}\int_0^1 \frac{d\lambda}{\lambda}\lim_{t'\to t^+}\lim_{\mathbf{r}'\to\mathbf{r}}\left[\int d\mathbf{y}\delta(\mathbf{r}_1 - \mathbf{y})\left(i\hbar\frac{\partial}{\partial t} - h_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{y})\right)\mathrm{Tr}\,G^{\lambda}(\mathbf{y}, t; \mathbf{r}_2, t')\right]. \tag{B6}$$

While Eq. (B6) is able to furnish a local definition of cor- relation energy density, the explicit determination of the

Green function $G^\lambda(\mathbf{r}_1, t; \mathbf{r}_2, t')$ represents a considerable challenge.

It is worth noticing that when the Green function is taken in the HF approximation, since the operator $\left(i\hbar\frac{\partial}{\partial t} - h_{\mathrm{HF}}\right)$ furnishes the inverse of this HF Green function, it follows that the correlation energy vanishes as it should do, since its definition is the difference between the exact energy E and the HF value E_{HF}. This property has an interesting implication. Let us assume that the correlation energy density defined in Eq. (4) has a dependence on $\mathbf{r}$ which closely follows the one associated of the HF density (or the exact one) [2]. Then, from definition (B6) it follows that the HF correction to the propagator does not contribute at all to the correlation energy. Therefore, the approximate validity of the correlation energy density formula proposed in [2] means that the contributions to the correlation energy density coming from the higher order corrections to the Green function, should approximately follow the behavior of either the total or the HF density. Therefore, the validity of the proposals of [2] for the correlation energy density, directly implies that the exact (or the HF) density should have a close relation with the exact or the HF densities. This conclusion arises because the higher corrections to the HF density turn to be approximately proportional to the same exact (or HF) densities as implied by the correctness of the definitions given in [2]. This property is supported by the analytical results of section III in which a close similarity between the HF electron density and the correlation energy density emerged. These general issues are expected to be analyzed in future extensions of the work.

Returning briefly to the theme of the correlation energy density $\epsilon_c(\mathbf{r}_1)$, we have written in Eq. (B6) a formula involving the Green function G^λ which can be brought into contact with a similar result for the level shift formula. Let us note that Eq. (B6), as well as Eq. (4), can always be rewritten in the form:

$$\epsilon_c(\mathbf{r}_1) = \int C(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \qquad (B7)$$

following a similar generalization for kinetic and exchange energy densities, but now in HF theory, proposed by March and Santamaria [17, 18]. Then the level shift (LS) formula, Eq. (4) reads

$$C^{\mathrm{LS}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\int \Psi^*[H - H_{\mathrm{HF}}]\Phi_{\mathrm{HF}} d\mathbf{r}_3 \dots \mathbf{r}_N}{\int \Psi^* \Phi_{\mathrm{HF}} d\mathbf{r}_1 \dots d\mathbf{r}_N}. \qquad (B8)$$

The conventional exact wavefunction (WF) theory reads

$$C^{\mathrm{WF}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\int \Psi^* H \Psi d\mathbf{r}_3 \dots d\mathbf{r}_N}{\int \Psi^* \Psi d\mathbf{r}_1 \dots d\mathbf{r}_N} - \frac{\int \Phi_{\mathrm{HF}}^* H \Phi_{\mathrm{HF}} d\mathbf{r}_3 \dots d\mathbf{r}_N}{\int \Phi_{\mathrm{HF}}^* \Phi_{\mathrm{HF}} d\mathbf{r}_1 \dots d\mathbf{r}_N}. \qquad (B9)$$

While, in general, these forms of $C(\mathbf{r}_1, \mathbf{r}_2)$ are different, they must all integrate to the same $\int \epsilon_c(\mathbf{r}_1) d\mathbf{r}_1$. This is true also for the two coupling constant integration formulae derivable from Eqs. (23) and (B6).

What we stress in this Appendix is the N-particle character of Eqs. (B8) and (B9), and the Green function generalization of $C(\mathbf{r}_1, \mathbf{r}_2)$ following from Eq. (B5). To date, of course, analytical progress is restricted to the Moshinsky atom. But since we have treated this fully in the body of the text, we shall omit further details.

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